

# REFRACTORIES FOR THE GLASS INDUSTRY

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## TECHNOLOGICAL ASPECTS OF SINTERING OF FINELY DISPERSE CHROMIUM OXIDE POWDERS

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Sintering of finely disperse chromium oxide powders was investigated. It was shown that dense poreless samples can only be obtained by incorporation of titanium oxide and firing in a carbon-containing charge. The optimum parameters of the manufacturing process were determined and technological regulations for the production of chromium oxide articles were developed. The technology was introduced in production.

The quality of glass for production of glass fiber is determined to a significant degree by the corrosion resistance of the refractory materials used, in addition to such process factors as homogenization and degassing of the glass melt, use of complex finely ground feedstock, and high boiling temperature. The aggressiveness of aluminoborosilicate glass melts (type E) makes it difficult to use traditional refractories in the tank lining of glass-making furnaces for production of glass fibers.

The resistance of different refractories to aluminoborosilicate glass (type E) is reported in Table 1 (US Patent No. 50213765) [1, 2]. The composition of E-glass is (%<sup>2</sup>): 53.0 SiO<sub>2</sub>, 15.0 Al<sub>2</sub>O<sub>3</sub>, 10.0 B<sub>2</sub>O<sub>3</sub>, 17.0 CaO, 4.0 MgO, 0.3 ΣR<sub>2</sub>O<sub>3</sub>, 0.1 Fe<sub>2</sub>O<sub>3</sub>, 0.6 other [3].

The data show that refractory articles made of chromium oxide have maximum corrosion resistance in an E-glass melt in the entire temperature range investigated. Dense articles made of finely disperse chromium oxide powders have very low heat resistance. Pastes consisting of a large-grain filler and finely disperse binder in the ratio of 70 : 30% are used to increase heat resistance. Granular densely sintered chromium oxide filler is not manufactured on industrial scales in our country. For this reason, we created technology for production of a dense granular chromium oxide filler.

To enhance sintering of chromium oxide, three methods of batch activation were used to obtain dense, poreless samples: fine grinding of chromium oxide powders, incorpora-

tion of a sintering additive (titanium oxide), firing in a reducing atmosphere.

Grade OKhM chromium oxide (GOST 2912–89), titanium oxide (GOST 9808–84), birch activated carbon — BAC (GOST 6217–784), graphite grit (TU 48-02-20–90), Kryptol (TU 48-46-15–95), and graphite electrode cullet (GOST 227898–98) were used in the study.

Chromium oxide was dry ground in a vibrating mill with metal beads to a minimum specific surface area of 5000 cm<sup>2</sup>/g. Milling was conducted with a sintering additive (4% titanium oxide). The total duration of milling was 1 h. The material : beads ratio was 1 : 10. The specific surface area was determined on an ADP-2 instrument.

TABLE 1

Refractory material	Weight losses, %		
	1320°C, 6 h	1420°C, 16 h	1550°C, 6 h
Based on chromium oxide	—	—	1.1–3.5
Melted baddeleyite – corundum	2.8–4.5	22.1–30.5	36.1–37.5
Based on aluminum oxide	6.0–7.3	—	60.4–65.5
Alumina-rich with zirconium additive	5.0–5.5	40.1–46.5	—
Kaolin	20.1–23.0	—	—
Chamotte	17.3–18.2	100.0	—
Based on molten quartz	3.2–4.5	17.0–18.1	30.0–32.8
Based on zirconium	—	5.1–7.2	39.0–40.3

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<sup>2</sup> Hear and below — the weight content.

TABLE 2

Molding pressure, MPa	Carbon-containing charge	Properties of samples after firing*		
		apparent density, g/cm <sup>3</sup>	open porosity, %	shrinkage, %
30	—	4.03	10.1	8.0
50	—	4.05	8.9	8.0
75	—	4.10	7.8	7.5
30	BAC	4.30	8.1	10.3
50	"	4.34	6.7	10.7
75	"	4.35	6.6	9.5
30	Graphite grit	4.32	7.5	10.2
50	Same	4.40	1.5	10.3
75	"	4.45	1.3	10.5

\* Firing temperature of 1550°C, holding time of 1 h.

The ground chromium oxide was moistened with a temporary binder (5% solution of polyvinyl alcohol in water) to a 6.0 – 6.5% moisture content of the paste. After moistening, the paste was passed through a rubbing screen with a 1 – 2 mm mesh size and left to ripen for 1 – 2 days after packing in 5-kg polyethylene packages. After ripening, samples 25 mm in diameter and 25 mm high were molded from the paste in a hydraulic press for conducting the studies. The samples were molded in a steel mold, ensuring bilateral molding, at different specific pressing pressures.

#### Effect of Molding Pressure on the Apparent Density of the Molded Pieces

Molding pressure, MPa	Apparent density of molded pieces, g/cm <sup>3</sup>
30 . . . . .	3.20
50 . . . . .	3.36
75 . . . . .	3.42

When the molding pressure was higher than 75 MPa, cracks appeared in the samples. Briquetting of the batch, two-stage molding, and other process methods did not produce defect-free samples in this case.

The samples were fired in an electric furnace with chromite – lanthanum heaters. The samples were sintered in corundum crucibles whose top was covered by a corundum lid. To keep oxygen from entering the crucible, the gap between the lid and the crucible was sealed with a refractory cement (clay + kaolin). A reducing atmosphere was created in the crucible in sintering the chromium oxide samples with a carbon-containing charge.

The results of the studies to assess the effect of the molding pressure and nature of the carbon-containing charge, firing temperature, and holding time at the maximum firing temperature on the properties of the samples are reported in Tables 2 – 4.

TABLE 3

Firing temperature, °C	Carbon-containing charge	Properties of samples** after firing		
		apparent density, g/cm <sup>3</sup>	open porosity, %	shrinkage, %
1500	—	3.88	13.8	7.0
	BAC	4.12	10.5	7.6
	Graphite grit	4.21	6.8	7.9
1550	—	4.00	10.1	6.5
	Graphite electrode cullet	4.25	9.2	8.0
	BAC	4.34	8.5	8.3
	Graphite grit	4.40	3.0	9.9
	Kryptol	4.90	1.0	12.7
1600	—	4.10	9.0	6.0
	BAC	4.40	8.3	8.2
	Graphite grit	4.76	1.0	10.3
	Kryptol	5.00	0.5	13.5

\* Held for 1 h.

\*\* Samples molded at a pressure of 75 MPa.

TABLE 4

Holding time, * h	Carbon-containing additive	Properties of samples** after firing		
		apparent density, g/cm <sup>3</sup>	open porosity, %	shrinkage, %
1.0	—	4.10	7.9	7.5
	BAC	4.34	8.5	8.3
	Graphite grit	4.40	3.0	9.5
5.0	—	4.25	7.5	7.1
	BAC	4.65	3.0	8.7
	Graphite grit	4.67	3.0	8.8

\* Firing temperature of 1550°C.

\*\* Samples molded at a pressure of 75 MPa.

These data show that the initial density of the semi-products and the nature of the carbon-containing additive affect sintering of chromium oxide.

Increasing the firing temperature caused the density of the samples to increase and the porosity to decrease regardless of the nature of the carbon-containing additive used to create the reducing medium. When Kryptol was used as the carbon-containing additive, the chromium oxide samples had a higher density after firing in comparison to the samples fired in other charges.

Increasing the holding time caused compacting of the chromium oxide samples regardless of the type of carbon-containing additive used.

The effect of the thickness of the carbon-containing charge layer on sintering of finely disperse chromium oxide

TABLE 5

Kryptol charge layer thickness, cm	Properties of samples		
	apparent density, g/cm <sup>3</sup>	open porosity, %	shrinkage, %
0.5	4.88	1.7	12.7
1.0	5.00	0.5	13.0
2.0	5.00	0.5	13.0

powder was investigated to work out all of the elements in the technology. Powder of the carbon-containing additive of defined thickness was poured on the bottom of a corundum crucible of the corresponding diameter and the molded chromium oxide sample was placed on it. The gap between the wall of the crucible and the sample, which was of the same size as the thickness of the charge on the bottom, was totally filled by the carbon-containing additive. A layer of carbon-containing powder of the thickness selected in the given experiment was poured on top of the sample. The effect of the charge layer thickness on the properties of the chromium oxide samples (1550°C sintering temperature, 1 h holding time, 75 MPa molding pressure) is reported in Table 5.

The results in Table 5 on sintering of finely disperse chromium oxide show that the optimum thickness of the carbon-containing charge must be determined in order to obtain dense, poreless samples. In our case, this thickness was 1 cm, i.e., such a volume of the carbon-containing additive was sufficient to create a reducing atmosphere that ensured densification of the finely disperse chromium oxide samples and prevented access of oxygen to the samples, which would make densification of the samples in sintering difficult.

Experiments on sintering in which the samples were not charged with a carbon-containing charge but were placed in a closed volume on a layer of fill of different thickness were conducted to simplify the technology. It was found that dense poreless samples could not be obtained with this technology.

Increasing the amount of sintering additive (titanium oxide) from 4 to 20% in sintering in an oxygen-containing atmosphere only caused insignificant densification of the samples (from 4.0 to 4.2 g/cm<sup>3</sup>). The composition of the samples after firing was spinellide of varying composition  $Ti_{n-2}Cr_2O_{2n-1}$  and  $Cr_2O_3$ . In firing in a reducing atmosphere (Kryptol), regardless of the amount of titanium oxide added, the density of the samples was 4.9–5.0 g/cm<sup>3</sup> and the mineral composition of the samples was spinellide of varying composition  $Ti_{n-2}Cr_2O_{2n-1}$ ,  $Cr_2O_3$ , chromium carbide, and dissemination of reduced metallic chromium.

Based on the results of the study, the technology was tested in industrial conditions on articles measuring 250 × 125 × 65 mm. In sintering in both periodic and in tunnel furnaces, dense chromium oxide articles were obtained. A technological regulation TR 11773998-4.2–2004 was developed for manufacturing sintered chromium oxide semiproducts.

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